

# PumpKin: A tool to find principal pathways in plasma chemical models

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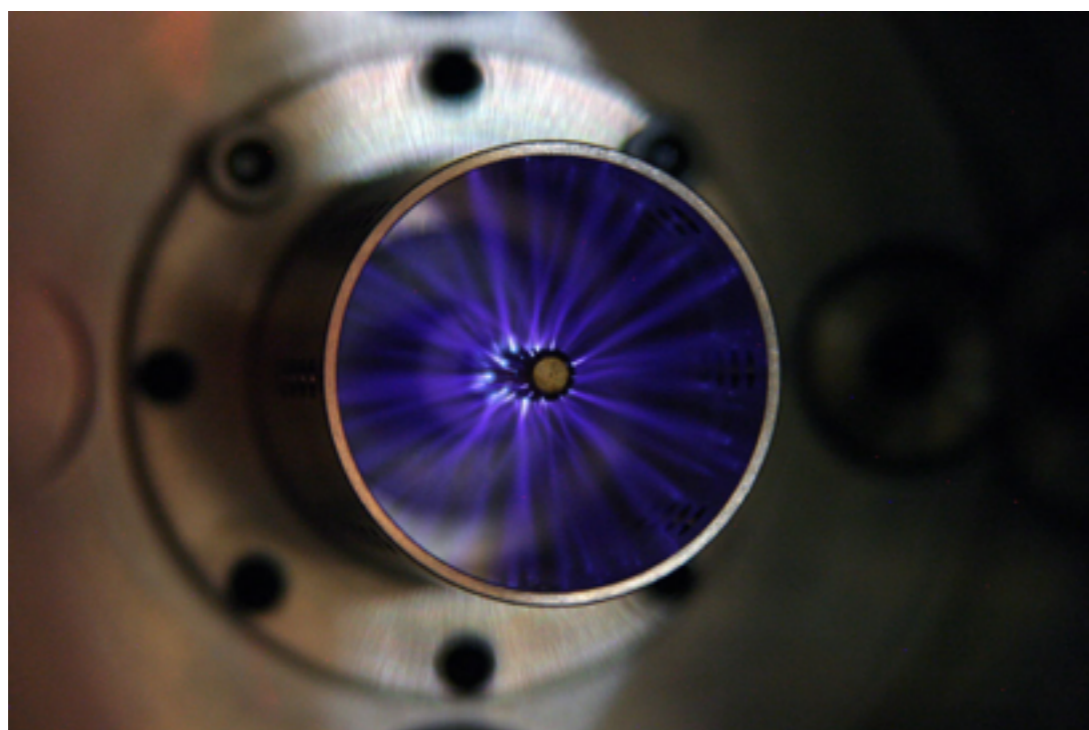
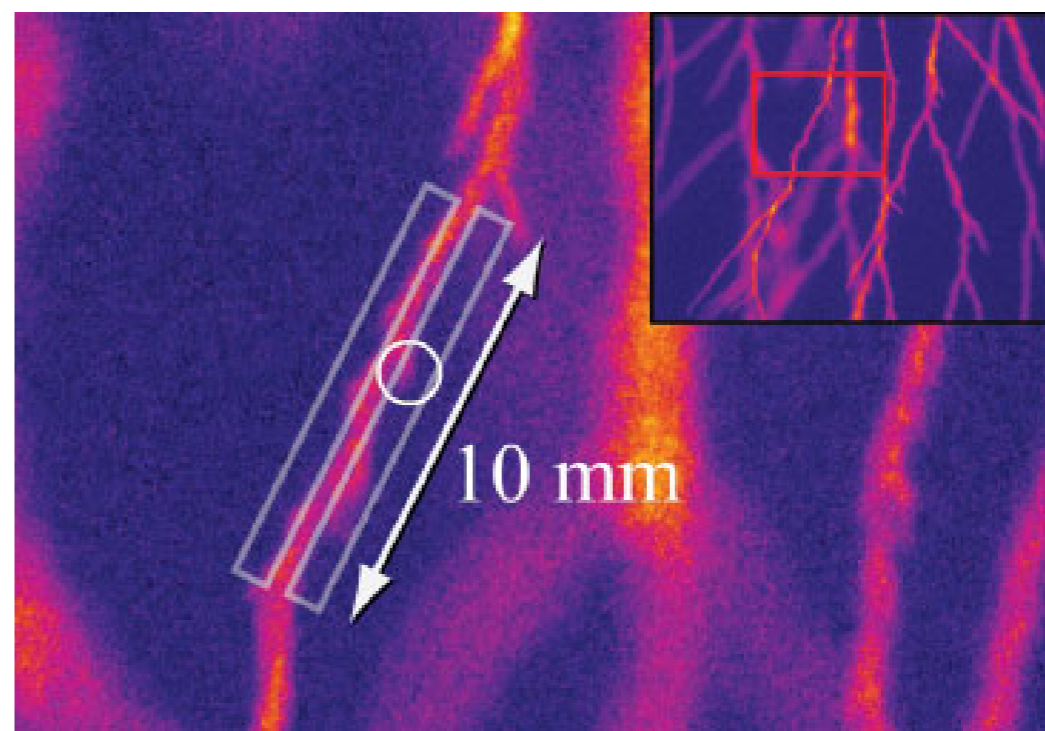
GEC

Princeton, October 1, 2013

# Outline

- Motivation
- PumpKin package
- Examples
- Where to get it?

# Plasma chemistry



# Plasma-chemical models

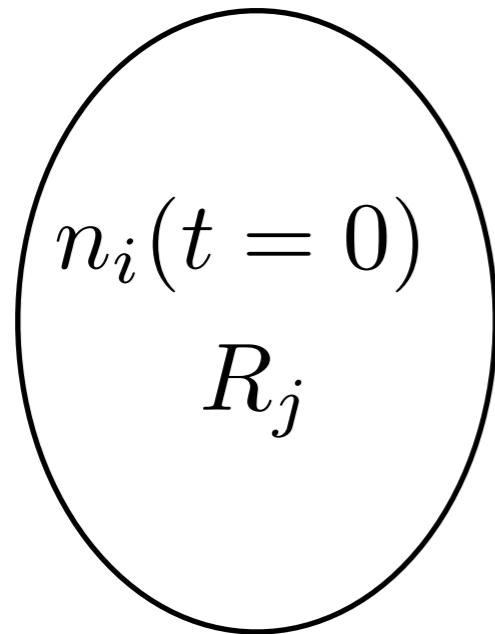
$$\frac{\partial n_i}{\partial t} = \overset{\text{gains}}{\downarrow} G - \overset{\text{losses}}{\downarrow} L$$

$n_i$  concentration of the atomic and molecular neutrals, ions, electrons

$G$  production rate of species  $n_i$  by all reactions

$L$  destruction rate of species  $n_i$  by all reactions

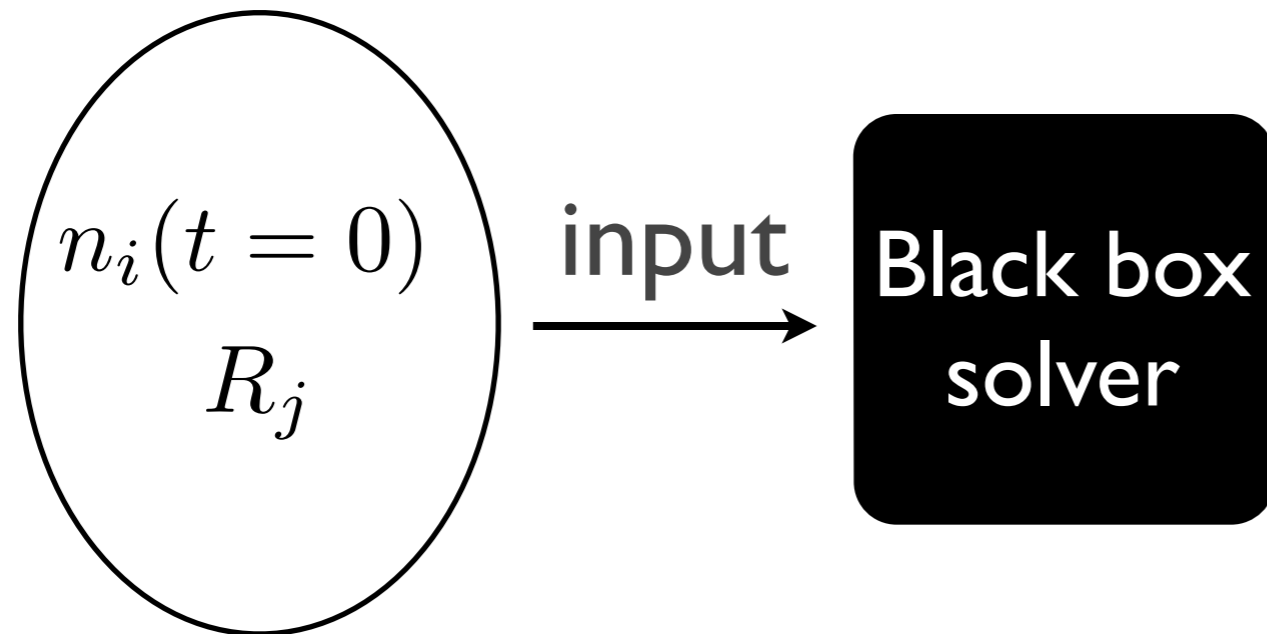
# Plasma-chemical models


$$n_i(t = 0)$$
$$R_j$$

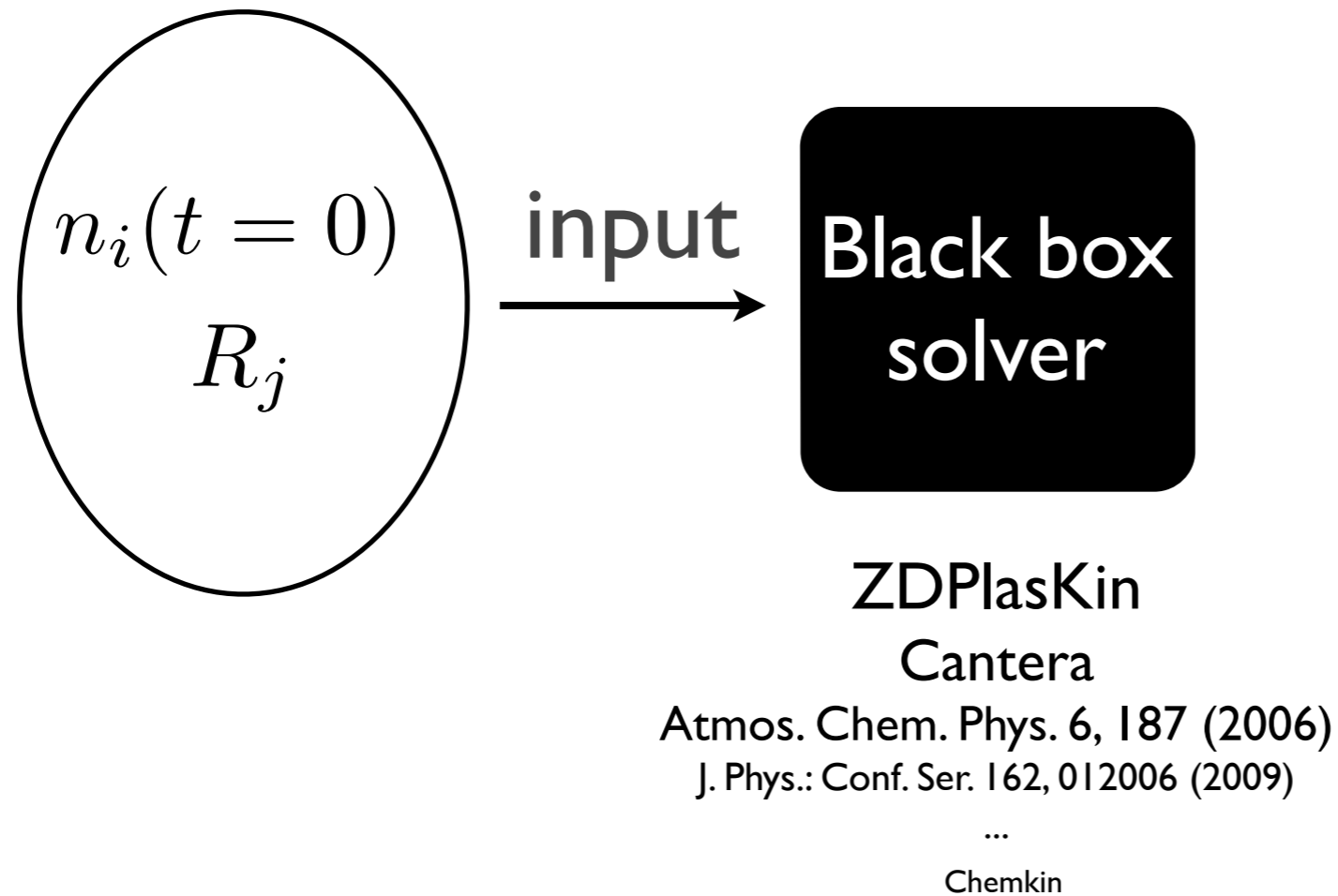
$i$  species index

$j$  reactions index

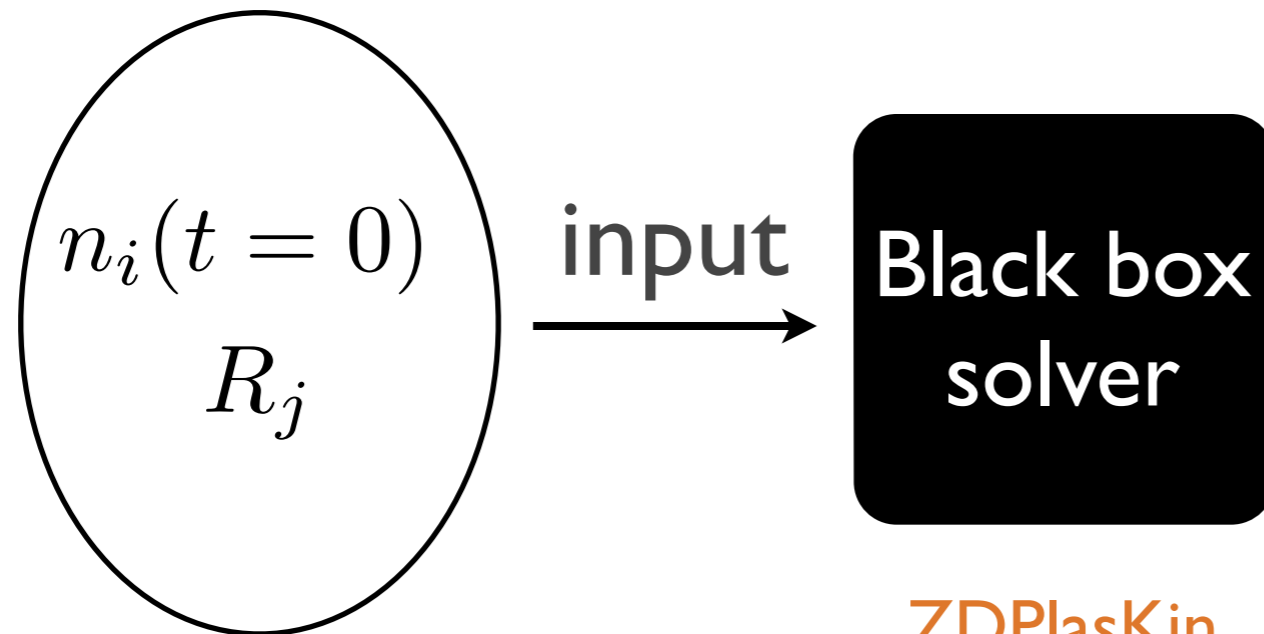
# Plasma-chemical models



# Plasma-chemical models



# Plasma-chemical models



ZDPlasKin

Cantera

Atmos. Chem. Phys. 6, 187 (2006)

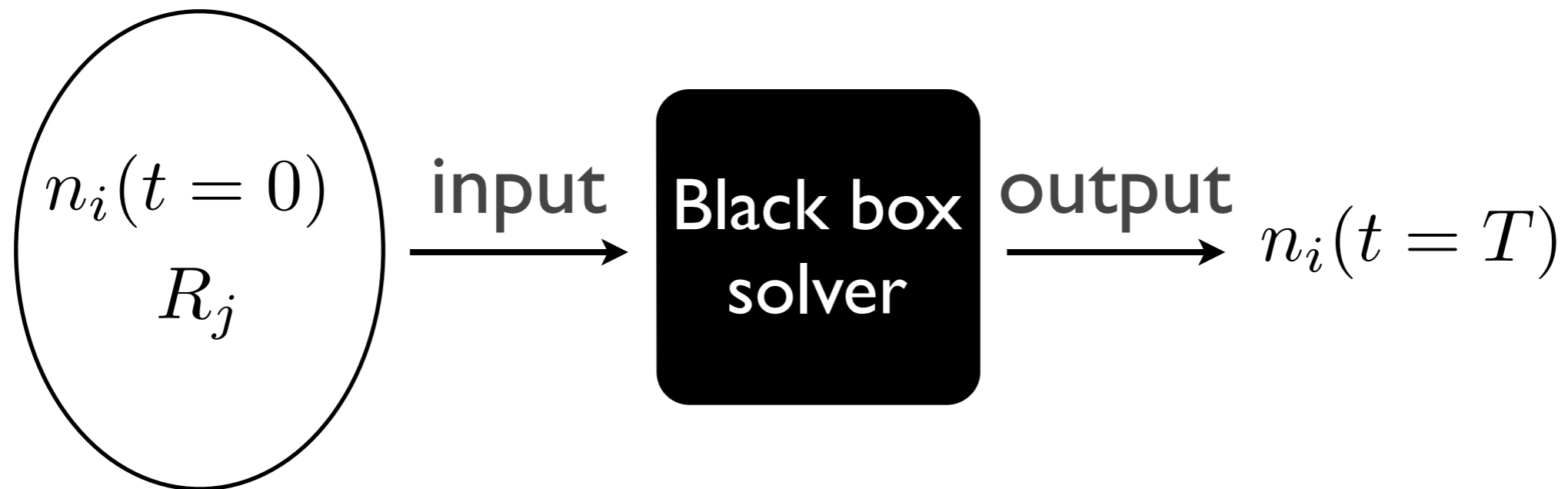
J. Phys.: Conf. Ser. 162, 012006 (2009)

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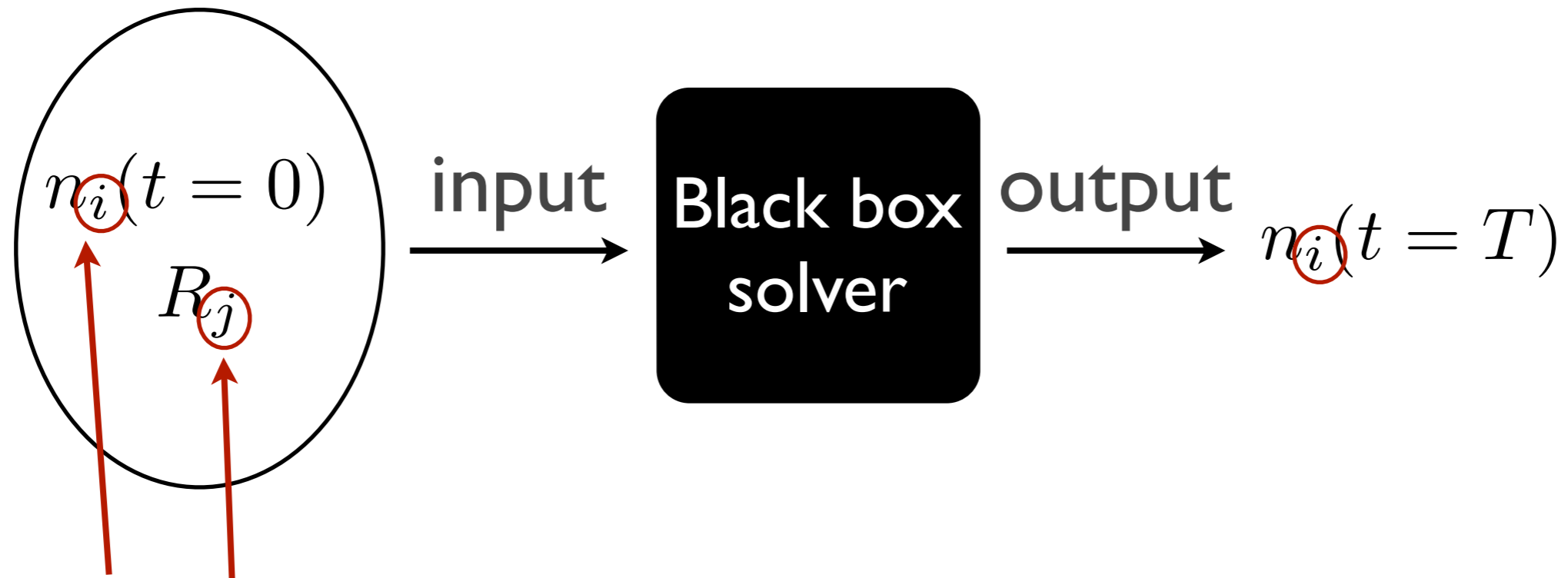
Chemkin



# Plasma-chemical models

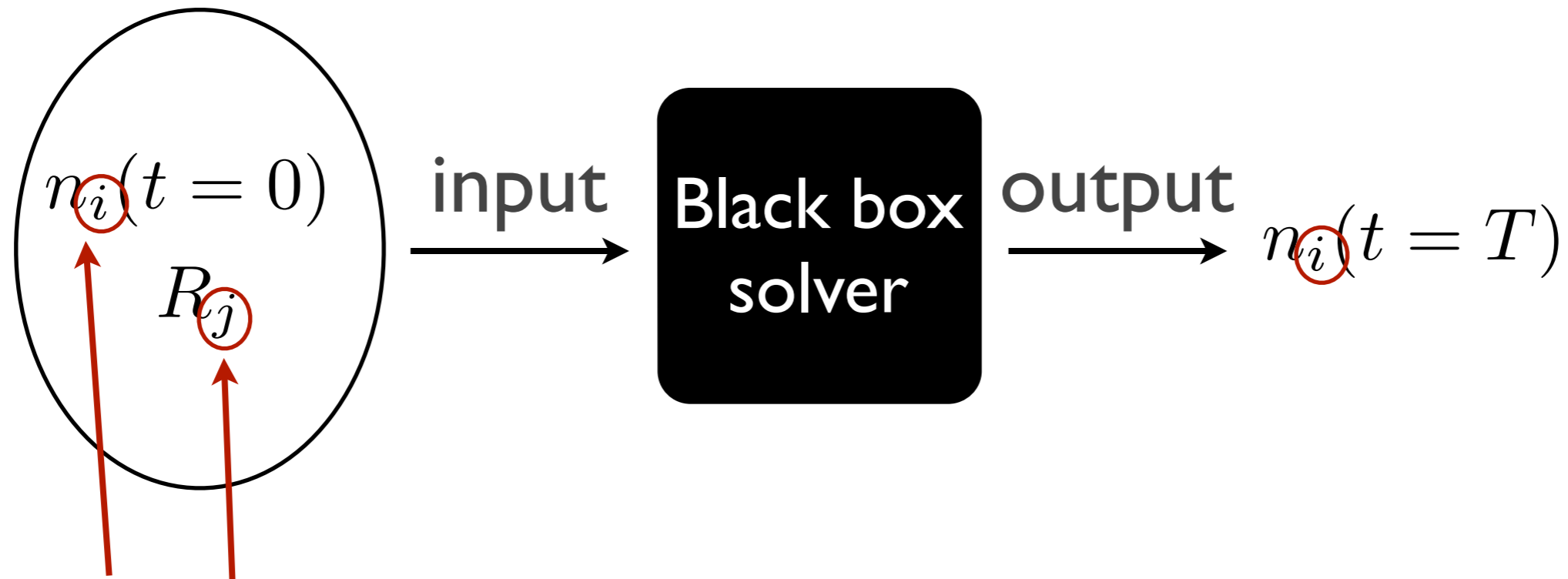


# Plasma-chemical models



Can be very big!

# Plasma-chemical models



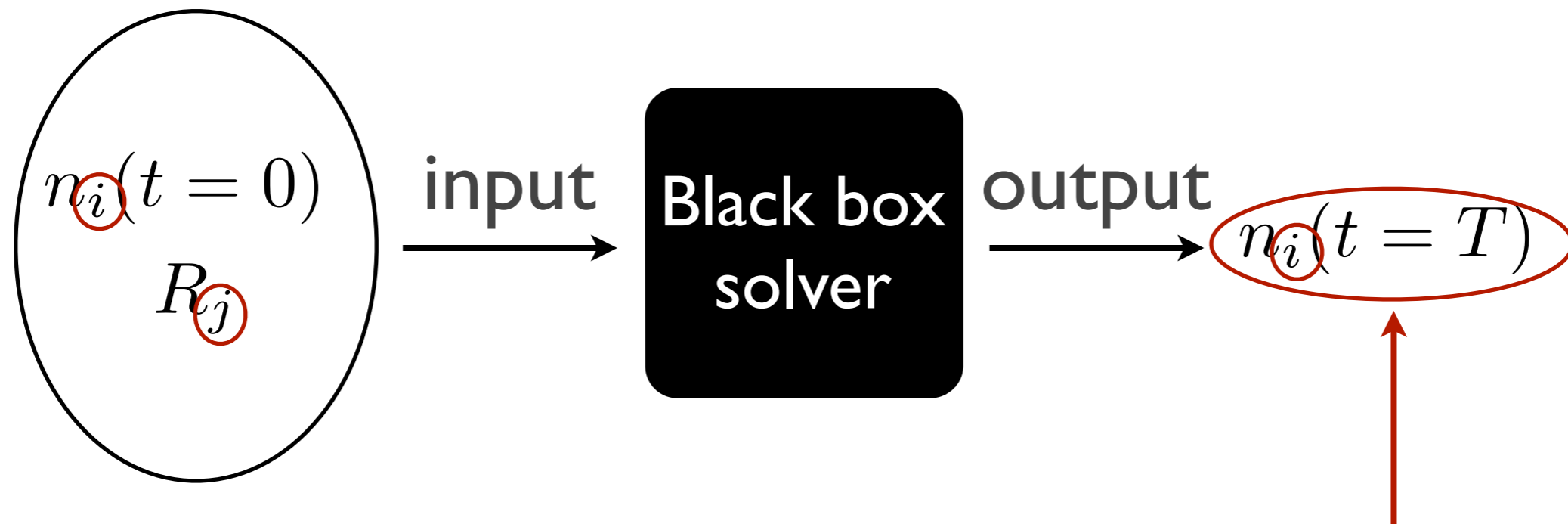
Can be very big!

- air (dry) plasma kinetics  $i = 75, j = 500$
- gas giant atmosphere  $i = 90, j > 2000$

1 F.J. Gordillo-Vázquez, J Phys D Appl Phys 41, 234016 (2008)

2. C. Bilger, P. Rimmer, and C. Helling, doi:10.1093/mnras/stt1378, (2013)

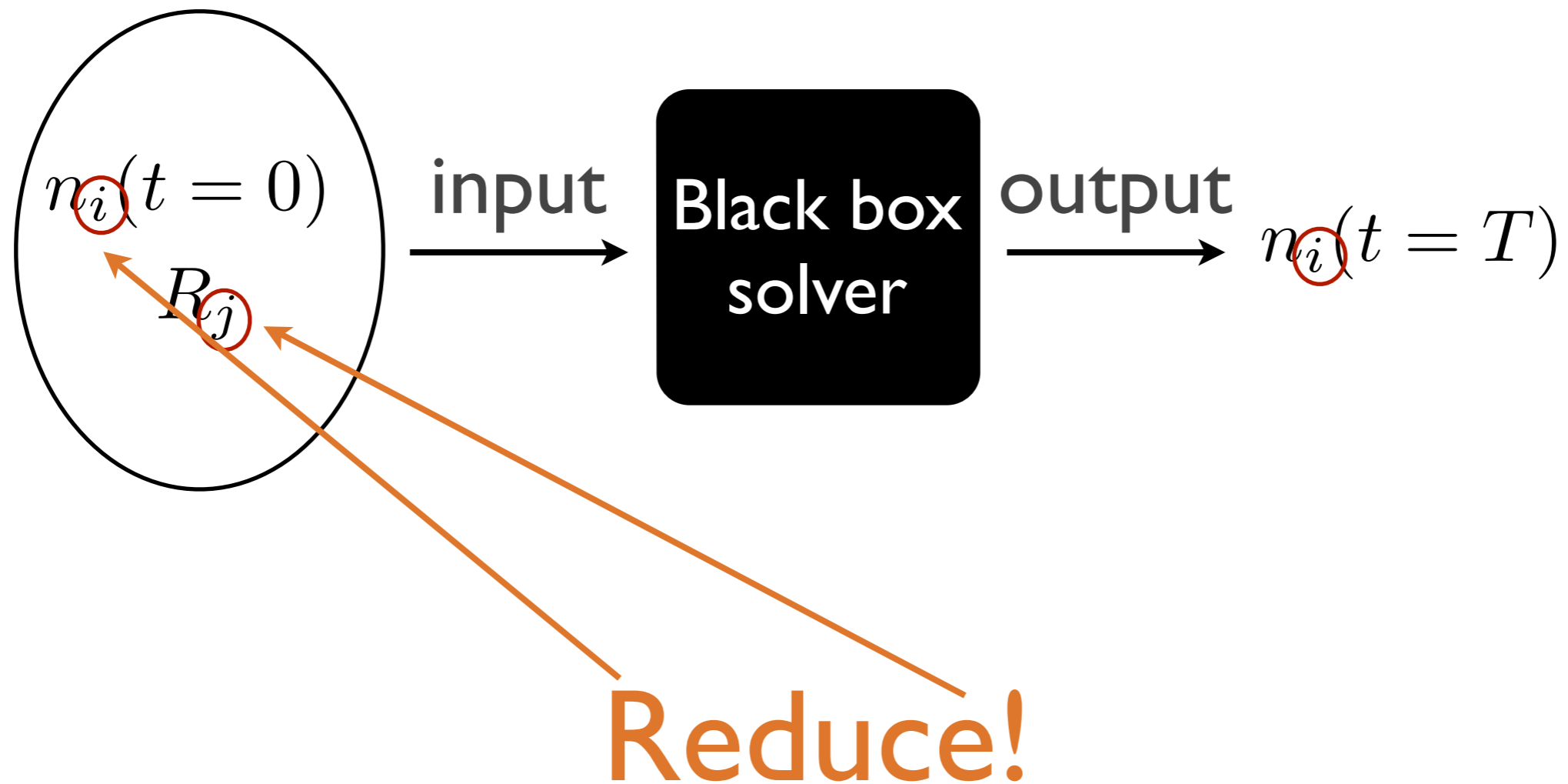
# Plasma-chemical models



How to understand?  
What to do with this?



# Plasma-chemical models



How?







No!

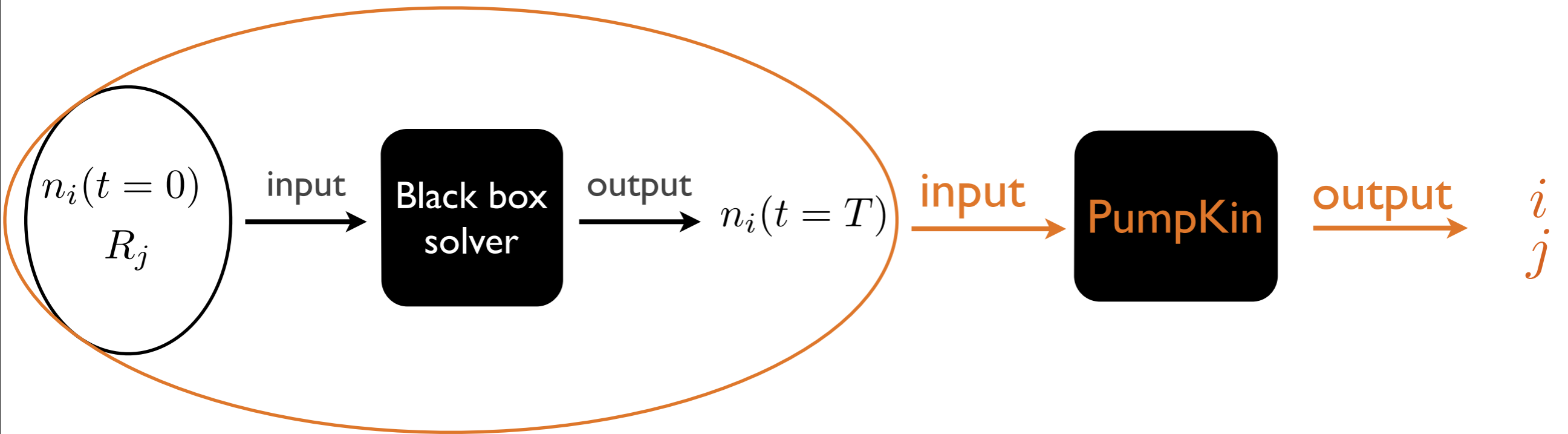
# PumpKin

(Pathway reduction method for plasma Kinetics)



PumpKin package

# PumpKin



Run only once!

# Input

- Stoichiometric matrix
- Concentrations of chemical species in  $[0, T]$
- Reaction rates in  $[0, T]$
- Time interval of interest  $(t_{\text{init}}, t_{\text{end}})$  in  $[0, T]$
- Species of interest  $S_{i^*}$ , if one

# Output

(\*)  
All significant pathways , with rates

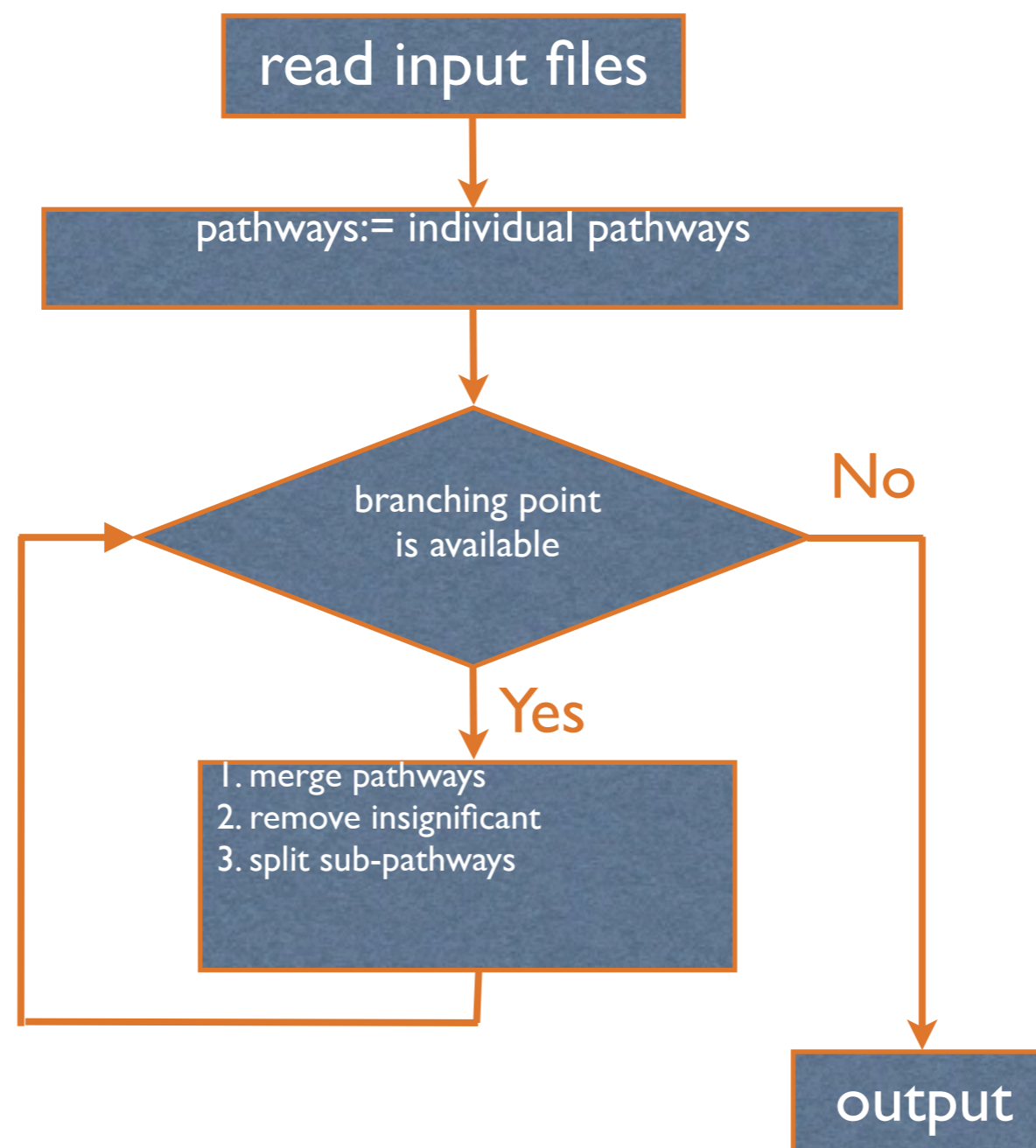


If  $S_{i^*}$  is specified, all pathways

- producing  $S_{i^*}$
- destroying  $S_{i^*}$

(\*) Pathway is a set of reactions, with a multiplicity assigned to each reaction

# How does PumpKin work?



1. Schuster & Schuster, 1993

2. Lehmann, 2004: *J. Atmos. Chem.* 47, 45-78.



# Example

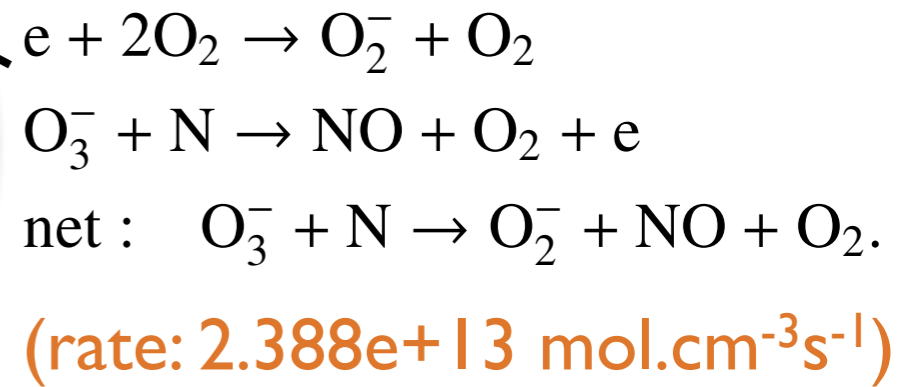
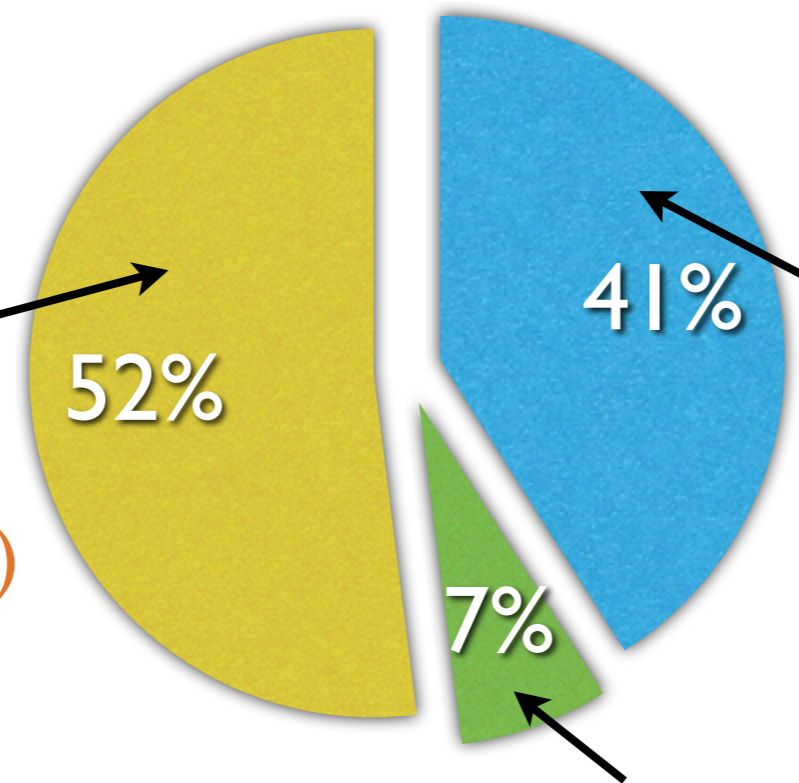
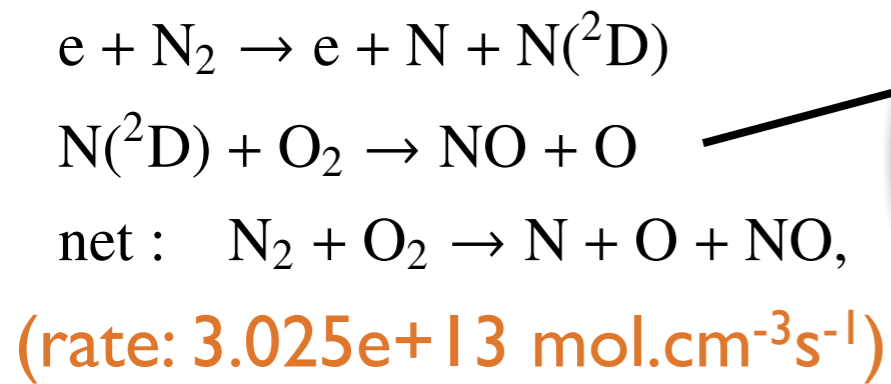
Zero-dimensional kinetics using ZDPlasKin (\*):

- N<sub>2</sub>-O<sub>2</sub> mixture 650 reactions and 53 species
- Fixed electric field 10 kV/cm at STP
- Final time: 1 ms
- Initial electron density 3.0e10 cm<sup>-3</sup>

(\*) S. Pancheshnyi et al., [www.zdplaskin.laplace.univ-tlse.fr](http://www.zdplaskin.laplace.univ-tlse.fr)

# Example

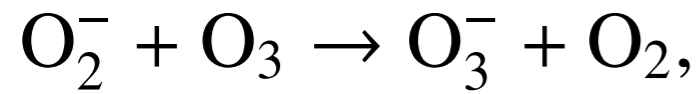
## NO production



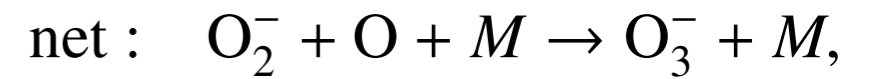
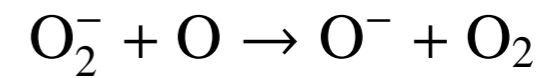
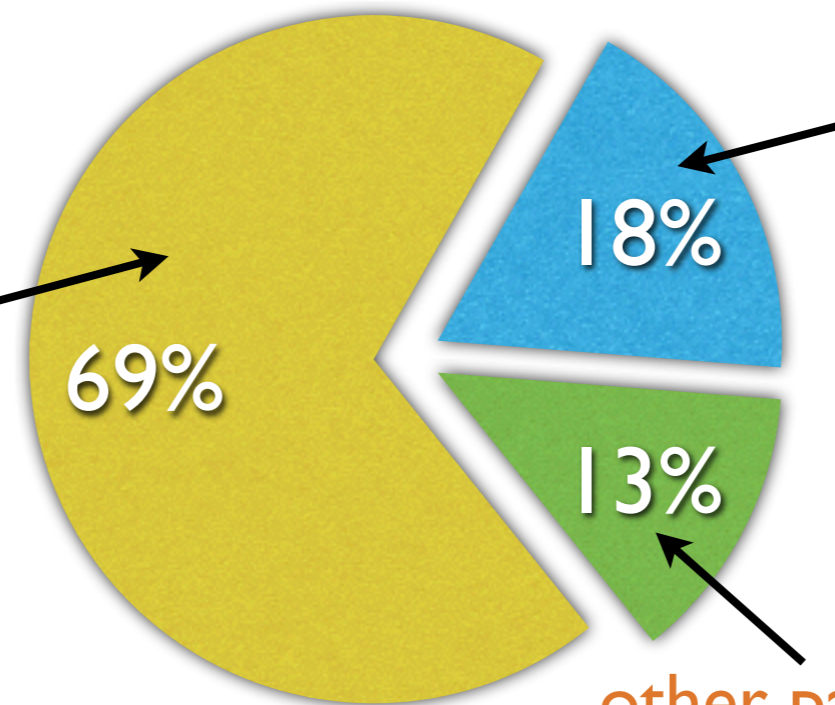
other pathways

# Example

## $O_3^-$ production



(rate:  $5.337e+16 \text{ mol.cm}^{-3}\text{s}^{-1}$ )

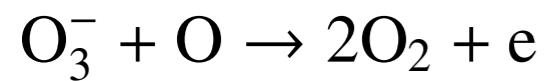
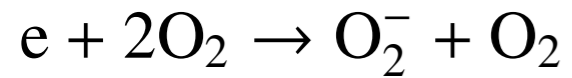


(rate:  $1.410e+16 \text{ mol.cm}^{-3}\text{s}^{-1}$ )

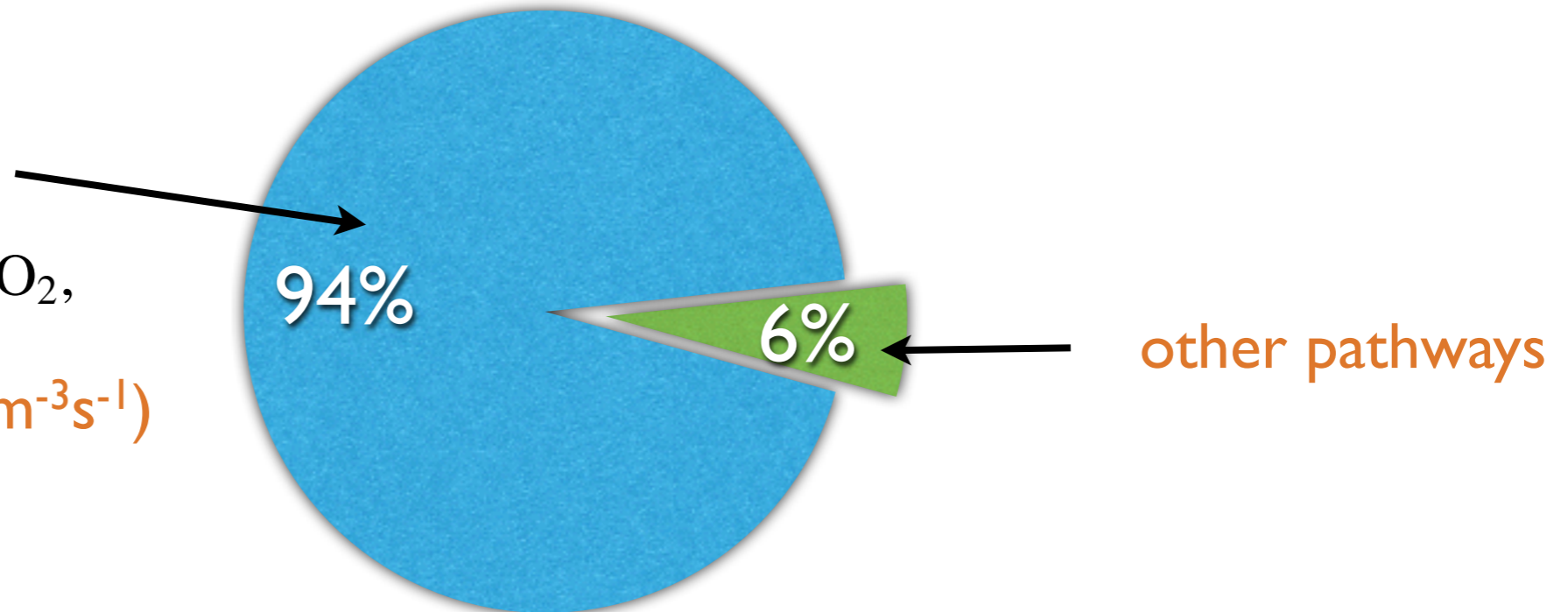
other pathways

# Example


## $O_3^-$ destruction



(rate:  $3.097e+16 \text{ mol.cm}^{-3}\text{s}^{-1}$ )




# How to get PumpKin?



## PumpKin: A tool to find principal pathways in plasma chemical models

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<sup>(1)</sup> CWI, Amsterdam, Netherlands, <sup>(2)</sup> IAA – GSIC, Granada, Spain.



### Introduction

We have developed a software tool called **PumpKin** (pathway reduction method for plasma kinetics) to find all principal pathways, i.e. the dominant reaction sequences, in chemical reaction systems. The goal is to explain, understand and eventually reduce complex plasma chemistry models. PumpKin is a universal tool, which only requires from the user the temporal profile of the densities of species and the reaction rates, as well the stoichiometric matrix of the system. Also, the user should specify the timescale of interest. Our approach is based on algorithm described in [9].

#### Physical model

The time evolution of the species densities in a system can be written as a set of coupled rate equations:

$$\frac{d[n_i]}{dt} = \sum_j R_{ij}(t),$$

where  $[n_i]$  is the density of species  $i = 1, \dots, N_s$  and the source term  $R_{ij}$  correspond to the contribution from different processes. Electron transport and rate coefficients can be obtained, for instance, from the BOLSAR+ solver.

Recently many non-commercial [1,2,3] and commercial [4] packages have been developed to follow the time evolution of the species densities and gas temperature in non-equilibrium plasmas with complex chemistry.

The typical output of [1] is the temporal evolution of reduced field, gas and electron temperatures, density of species, reaction source rates and reaction specific production rates of species for sensitivity analysis. Depending on the complexity of the chemical model, output can be around 100 Mb of raw data.

Tools like QP/QPcode [5] are developed to analyse the results from a plasma kinetic code such as ZEPHYRUS [6] in a GUI graphical user interface.


**Kinetics**

↓

**Solver**  
(pathways, stoichiometric)

↓

**Results**  
(paths)



#### PumpKin tool

The growing interest in plasma chemistry significantly increases the complexity of chemical models. Recent kinetic models of atmospheric chemistry [7] or of industrial applications [7] contain thousands of chemical reactions and species. Thus one should take into consideration that different species have different lifetimes, reaction reaction rates depend on externally applied electric field as well as on temperature. As a result, reactions and species are hard to be able to reduce the chemical reaction system to more compact chemical pathways, which will have much less reactions and will consider less species. For example, such techniques have been successfully applied to atmospheric chemistry to investigate ozone destruction [8].

In the present work we have developed the software PumpKin to find all principal pathways, i.e. the important reaction sequences. The user should solve first the full chemical reaction system, but only once. The output is later used as an input for PumpKin. Description of PumpKin algorithm is the following:

**begin**

read input file

initialize pathways = individual pathways

**repeat**

choose last species  $k$

merge pathways producing  $k$  with pathways containing  $k$

delete independent pathways

deconstruct and split sub-pathways

**until** there are no last species  $k$  remaining

**end**

**Example**

As an example, we take the air ( $N_2/O_2 = 80/20$ ) at 917 [1]. We use ZEPHYRUS plasma kinetic solver to simulate gas-discharge kinetics. Maximum electric field is 300 Td and pulse duration is 100 ns. Simulation total duration is 1  $\mu$ s. We use kinetics from [1], containing 30 species and 104 reactions. The time-dependent electric field is obtained, initial electron density is taken as  $5 \cdot 10^{17}$  cm<sup>-3</sup>. We choose NO as the specie of interest.

Reduce kinetics

Explain mechanism

Analyse kinetics

#### Reduce

If the user has no specific in the specie of interest, then he/she can specify the maximum number of the most important pathways (or reactions). For a given simulation time interval, PumpKin will return the most important pathways (sorted by the rate of pathway). For example, in the time interval of [100-2, 1.0e-3] the less 17 pathways of output are:

$$\left. \begin{aligned} O_2^+ + N_2 &\rightarrow O_2^+ + N_2 \\ O_2^+ + O_2 &\rightarrow M \rightarrow O_2^+ + M \\ O_2^+ + O_2 &\rightarrow O_2^+ + M \\ O_2^+ + O_2 &\rightarrow O_2^+ + M \\ O_2^+ + O_2 &\rightarrow O_2^+ + M \\ O + O_2 + N_2 &\rightarrow O_2 + N_2 \\ O + 2O_2 &\rightarrow O_2 + O_2 \\ O(1D) + O_2 &\rightarrow 2O \\ O_2 + O &\rightarrow O_2 + O \\ O_2(1D) + N_2 &\rightarrow O_2(1D) + N_2 \\ O_2(1D) + O &\rightarrow O_2 + O \\ + 3O_2 &\rightarrow O_2 + O_2 \\ O_2^+ + M &\rightarrow O_2 + M \end{aligned} \right\} 17$$

#### Explain

If the user is interested in a specie like NO in gas discharge plasma after 1.0e-3s, then all kinetics can be reduced down to the following 7 reactions, out of total 104:

$$\begin{aligned} N(2D) + O_2 &\rightarrow NO + O \\ \text{Production: } &+ 2O_2 \rightarrow O_2^+ + O_2 \quad 90.3\% \\ &O_2^+ + N \rightarrow NO + O_2 + e \end{aligned}$$


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$$\text{Net: } N(2D) + O_2 + O_2 + N \rightarrow 2NO + O_2 + O + e$$
  

$$\begin{aligned} O_2^+ + NO &\rightarrow NO_2^+ + O_2 \\ \text{Destruction: } &O_2^+ + O_2 + M \rightarrow O_2^+ + M \quad 89.7\% \\ &O + NO + N_2 \rightarrow NO_2 + N_2 \\ &N + NO \rightarrow O + N_2 \end{aligned}$$


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$$\text{Net: } 2NO + O_2^+ + N \rightarrow NO_2^+ + NO_2 + N_2$$

#### Analyse

Let us assume that the user is still interested in NO and wants to understand production/destruction during different time intervals. As an example, we show production/destruction after 1.0e-7 s. In this case all kinetics can be reduced down to the following 7 reactions:

$$\begin{aligned} \text{Production: } &N(2D) + O_2 \rightarrow NO + O \quad 100\% \\ &O_2^+ + NO \rightarrow NO_2^+ + O_2 \\ &O_2^+ + O_2 + M \rightarrow O_2^+ + M \\ \text{Destruction: } &O + NO + N_2 \rightarrow NO_2 + N_2 \quad 91.8\% \\ &N + NO \rightarrow O + N_2 \\ &O_2^+ + NO \rightarrow NO_2^+ + O_2 \\ &O_2^+ + NO + M \rightarrow NO_2 + M \end{aligned}$$


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$$\text{Net: } (NO + NO_2^+ + N \rightarrow O_2^+ \rightarrow NO_2^+ + 2O_2 + NO_2 + N_2 + NO_2)$$

#### References

[1] A. Pechoucky, B. Eganov, GJM. Hagston, I.C. Phillips 2008, Computer code ZEPHYRUS, <http://www.zephyrus.org.uk>

[2] G.D. Carter, P.D. Brugg, 2013, *Computer Physics Communications* 185, 191-197

[3] S.K. Prasad, J. Phys.: Conf. Ser. 182, 012001 (2009)

[4] R.J. Kee, J. Miller, F. Ripley, E. Meeks, 1996, *Chemkin*.

[5] A. Luque, QP/QPcode solver, <http://www.iaa.es/iaa/iaa/iaa/>

[6] F.J. Gordillo-Vázquez, *J. Phys. D: Appl. Phys.* 40, 234010 (2007)

[7] K. Fehsenfeld, *Plasma Chemistry*, Cambridge University Press, Cambridge, New York, 2000.

[8] J.L. Gonzalez, R. Williams, P. Merle, U. Langermann and B. Snel, *J. Geophys. Res.* 111, U1111 (2006)

# How to get PumpKin?

Available soon at: [www.pumpkin-tool.org](http://www.pumpkin-tool.org)

Thank you!